δ^2H Analysis of Methane via GC-IRMS

1. Introduction

The determination of the D/H ratio on methane has been historically used in combination with the $^{13}C/^{12}C$ ratio of methane to genetically type natural gases as being of thermogenic, mixed or bacterial origin (e.g., Schoell, 1980). In order to provide timely, accurate and precise hydrogen isotopic analyses, we utilize the latest continuous-flow technology to link a gas chromatograph to a modern isotope ratio mass spectrometer via a pyrolytic interface. All stable isotope methods employed by the Energy Geochemistry Laboratory follow the best practices and procedures as detailed in peer-reviewed literature.

2. Interfaces with Other Methods

None required.

3. Materials and Equipment

As described below in the Procedure.

4. Procedure

The D/H ratio of methane is determined using methods modeled after Burgoyne and Hayes (1998). A natural gas sample is introduced into a HP[1] 6890 gas chromatograph via an autosampler through a sample-loop injector. Methane is chromatographically separated on a Restek Rt Aluminabond KCl column (50 m x 0.32 mm). Typical GC conditions are as follows: He carrier gas @ 1 ml/min; 35 °C initial temp; hold for 12 min; ramp to 225 °C at 25 °C/min; hold for 5 min. The eluent methane is then pyrolyzed in the He stream at 1450 °C in an in-line Alsint-99.7 ceramic reactor (0.5 mm I.D. x 6 mm O.D. x 500 mm length). The resulting H_2 analyte is passively drawn

[1] Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

via open split into the source of a GV-Elementar Isoprime isotope ratio mass spectrometer for subsequent hydrogen isotope analysis.

5. Calibration and Quality Control Samples

Raw delta values from the instrument (IonVantage Software) undergo off-line isotope corrections for drift (as many batch runs take more than 24 hours to complete), for isotopic linearity due to the physical chemistry of the ceramic pyrolysis reactor (13C vs amount), and finally are normalized to the internationally-accepted SMOW-SLAP hydrogen isotope scale using two calibrated, working laboratory methane standards (after Paul et al, 2007). On average, for every 5 samples run in replicate (n = 5, 25 total determinations), ~50 analyses of standards are performed to ensure proper analytical calibration. The final hydrogen isotope values represent the average of multiple replicate analyses (n=5). All final δ^2H values are presented relative to the international standard, Vienna Standard Mean Ocean Water (VSMOW).

6. Limits, Precautions, and Interferences

Sample requirements are as such: pressurized gas cylinder/bottle (50-100mL) containing 15-75 psi of total gas with a minimum methane concentration of 10 mole percent. Samples may have high pressure and considerable concentration of hydrogen sulfide and should be handled with caution.

7. Acceptance of Data

Data are deemed acceptable if standard methane and working standards are within acceptable parameters (peak response (area or height), isotopic value and precision). The accuracy of isotopic measurements is normally not cited. However, as we utilize a two-point calibration, the accuracy of these determinations is expected to be within 2x the standard deviation. As replicate analyses are usually better than 2.0 ‰ standard deviation, we expect our accuracy to be better than 4 ‰.

8. Data Handling and Transfer

The following data are returned to the submitter: Sample ID, $\delta^2H_{(SMOW)}$, std, n; where Sample ID is the sample descriptor provided by the submitter, $\delta^2H_{(SMOW)}$ is the average methane hydrogen isotope value for the sample, std is the standard deviation in per mil of replicate analyses and n is the number of replicate analyses. An example of a final results data table is shown below.

Sample ID	$\delta^2H_{(SMOW)}$ ‰	stdev ‰	n
Pionce #24H	-225.4	0.5	5

Finally, data are submitted to the USGS Geochemical Database for general dissemination as per Energy Geochemistry Laboratory QA protocol.

9. References

Burgoyne T.W., and Hayes, J.M., 1998. Quantitative production of H_2 by pyrolysis of gas chromatographic eluents: *Analytical Chemistry*, v. 70, no. 24, p. 5136-5141.

Paul D., Skrzypek G. and Forizs, I., 2007. Normalization of measured stable isotopic compositions to isotope reference scales – a review. *Rapid Communications in Mass Spectrometry*, v. 21, p.3006-3014.

Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins: *Geochimica Cosmochimica Acta*, v. 44, p. 649-661.

10. Attachments

None.

11. History of Changes

R0: Initial Issue